

Heavy metal content in different types of smoked meat in Serbia

Snežana S. Mitić, Milan B. Stojković, Aleksandra N. Pavlović*, Snežana B. Tošić and Milan N. Mitić

Faculty of Sciences and Mathematics, Department of Chemistry, University of Niš, Višegradska 33, Serbia

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Concentrations of Fe, Cu, Ni, Cr, Pb, Mn, Zn and Cd in pork, beef, turkey and chicken samples were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). The mean concentration ranges in milligrams per 100 g of the studied metals in all samples were 0.6924–1.2154 for Fe, 0.6492–0.9831 for Cu, 0.0012–0.0027 for Pb, 0.041–0.0510 for Ni, 0.1186–0.1481 for Mn, 0.7257–5.2726 for Zn and 0.0042–0.0050 for Cd. The levels of analysed elements were in accordance with European standards for all metals except for manganese in all samples and for nickel in a certain number of samples. Zn level in beef was significantly higher compared to other samples, and Pb and Cd were found in concentrations well below the recommended daily intake.

Keywords: smoked meat samples; heavy metals; contamination; validation

Introduction

In addition to being a primary source of proteins in human diet, meat also contains certain amounts of macro and trace elements, including K, Na, Ca, Mg, Cu, Fe, Ni, Co, Mn, Cr, Hg, Pb, Cd and P. These elements are known to have a large influence on human health, effecting a wide variety of body functions, for example, enzyme function, osmotic pressure control, muscle contraction, etc. (Honikel 1999; Murray et al. 2003; McAfee et al. 2010). Although meat is not the only or even a primary source of these elements, their presence in most meat types is a significant addition to daily intake (Higgs 2000; Lombardi-Boccia et al. 2005).

Various amounts of the elements mentioned are naturally present in meat. However, the mostly negative human influence on ground, air and water has led to a somewhat diminished state of environmental conditions which, through the food chain, may affect the macro and trace element contents of meats (Demirezen and Askoy 2004). In recent years, much attention has been focused on the concentrations of heavy metals in food in order to check for those hazardous to human health. The influence is most obvious concerning the following elements, which are commonly considered a health risk: Hg, Pb and Cd (Zahir et al. 2005; Pedersen and Lierhagen 2006; Rudy 2009).

Pork, beef, turkey and chicken are some of the most popular meat types produced and used in Serbia. The oldest method of meat conservation still widely used is simple salting and drying of meat. This type of

processing requires little investment in time and resources.

Content of dried meats, in terms of organic composition as well as the amount of the above elements present, varies depending on multiple factors. Meat of different livestock types naturally has different properties. Meat sample composition will vary even within the same animal species if the livestock is not grown in the same region and under the same nutritional programme.

Another factor that must be taken into account is the drying process itself. First and foremost, meats dried under different conditions do not contain the same amount of moisture.

The most commonly used methods for analysing metals in meat samples are flame atomic absorption spectrometry (FAAS) (Abou-Arab 2001; Tomović et al. 2011), inductively coupled plasma-mass spectrometry (ICP-MS) (Yeats et al. 1999; Kosanovic et al. 2007) and inductively coupled plasma-optical emission spectrometry (ICP-OES) (Ferreira et al. 2000; Baranowska et al. 2006; Demirezen and Uruc 2006).

The objective of the present study is to provide a detailed determination of the contents of Fe, Cu, Ni, Cr, Pb, Mn, Zn and Cd in smoked meat samples of pork, turkey, beef and chicken consumed in Serbia.

Material and methods

Reagents

Nitric acid 65% was purchased from Merck (KGaA 64271; Darmstadt, Germany). Ultra scientific

*Corresponding author. Email: aleksandra.pavlovic@pmf.edu.rs

(N. Kingstown, USA) ICP multi-element standard solution of about 20.00 ± 0.10 mg/L was used as a stock solution. Deionised water ($0.15 \mu\text{S}/\text{cm}$) was obtained from MicroMed high-purity water system (TKA Wasseraufbereitungssysteme GmbH, Niederelbert, Germany).

Instrumentation

All analyses were carried out on an iCAP 6000 inductively coupled plasma-optical emission spectrometer (Thermo Scientific, Cambridge, United Kingdom) which uses Echelle optical design and a Charge Injection Device (CID) solid-state detector. The analytical lines used for each element, as well as the instrumental conditions are given in Table 1. The emission lines selected for each element are based upon tables of known interferences; baseline shifts and experience refer to work with different samples.

Dry ashing method was carried out in a VIMS electric (Serbia) furnace equipped with microprocessor's programmatic of temperature IVIGOS3123 ($\pm 1^\circ\text{C}$).

Meat samples

Five samples of each meat type (pork, beef, turkey and chicken) were obtained from different sellers at the local markets of the city of Nis, Serbia. All samples were obtained from well-known domestic producers on the same day, put into identical plastic containers and immediately transported to the laboratory.

Sample treatment

Samples were treated according to procedure given by Tomović et al. (2011) with certain modifications. Each sample was cut into small pieces with a stainless steel knife. The exact mass of each sample (10.000 g) was

weighed into a porcelain crucible and dried in a laboratory oven at 105°C for 3 hours. Afterwards, the samples were ashed in a furnace for 20 hours. The furnace was programmed to raise the temperature from starting 50 to 450°C in the first 8 hours, after which it was kept at a constant 450°C until the end of the process. The ash was dissolved in 2.5 mL of concentrated nitric acid/deionised water (1:1 v/v) and diluted to 50 mL using deionised water. Samples were then analysed using ICP-OES in order to determine presence and amounts of Cu, Fe, Ni, Mn, Cr, Pb, Cd and Zn.

Validation

The validation process of the measurements based on the ICP-OES technique involved linearity of the calibration curve and limits of detection and quantification (Table 2) and the spike recovery test results, which are included in the database. Linearity was assessed by the correlation coefficients of calibration curves. Detection (LOD) and quantification (LOQ) limits were calculated as $\text{LOD} = 3 \times \text{SD}/m$ and $\text{LOQ} = 10 \times \text{SD}/m$, respectively, where SD is the standard deviation of blank responses and m is the slope of the calibration graph.

Statistical analysis

The results were further analysed using ANOVA. LSD multiple range test was used in order to compare mean descriptor values.

Results and discussion

The metal content in different smoked meats was determined and carefully scrutinised. The results are given in the database, expressed in milligrams per 100 g wet weight, were obtained from triplicate measurements and rounded up to the last significant figure associated with random error (Supplementary Data). Mean values of iron, copper, chromium, lead, nickel,

Table 1. Operational ICP-OES parameters.

| | |
|----------------------|-----------|
| Flush pump rate | 100 rpm |
| Analysis pump rate | 50 rpm |
| RF power | 1150 W |
| Nebuliser gas flow | 0.7 L/min |
| Coolant gas flow | 12 L/min |
| Auxiliary gas flow | 0.5 L/min |
| Plasma view | Axial |
| Detection wavelength | nm |
| Cd | 228.802 |
| Cr | 357.869 |
| Cu | 324.754 |
| Fe | 259.94 |
| Mn | 257.618 |
| Ni | 341.476 |
| Pb | 220.353 |
| Zn | 213.856 |

Table 2. Detection (LOD) and quantification (LOQ) limits and correlation coefficients of the calibration curve for each element.

| Element | LOD mg/100 g | LOQ mg/100 g | Correlation coefficient |
|---------|-----------------|-----------------|----------------------------|
| Cd | 0.0009 | 0.0031 | 0.99981 |
| Cr | 0.0006 | 0.0019 | 0.99987 |
| Cu | 0.1927 | 0.6225 | 0.99999 |
| Fe | 0.1635 | 0.5446 | 0.99851 |
| Mn | 0.0245 | 0.0816 | 0.99847 |
| Ni | 0.0113 | 0.0344 | 0.99981 |
| Pb | 0.0003 | 0.0009 | 0.99918 |
| Zn | 0.1897 | 0.6317 | 0.99962 |

manganese, zinc and cadmium concentration in pork, beef, chicken and turkey samples are given in Table 3. Data obtained by analysis of all samples (20 different smoked meat products) put the average trace element levels into the following decreasing order: $\text{Zn} > \text{Fe} > \text{Cu} > \text{Mn} > \text{Ni} \sim \text{Cr} > \text{Pb} > \text{Cd}$.

From the experimental results, it can be concluded that zinc and iron are present in the highest concentrations. According to ANOVA, zinc content in dark meat samples (beef samples) is significantly higher in comparison to other samples ($p < 0.0001$). The average values of zinc concentration range from 0.7257 mg/100 g for chicken samples to 5.2726 mg/100 g for beef samples. World Health Organization (WHO 1993) establishes the maximum proposed concentrations of Zn in chicken, pork, beef and turkey at 8.5, 60, 40 and 20 mg/100 g wet wt, respectively. Therefore, the amounts of Zn found in our samples were still well below those limits, even for dark meat samples.

As with zinc, higher iron content was found in dark meat samples. The average concentration of Fe ranged from 0.6924 mg/100 g for turkey samples to 1.2154 mg/100 g for beef samples. Fe content in beef meat samples was significantly higher than the content of the metal in turkey meat samples ($p = 0.0159$), according to ANOVA. According to WHO (1993), on the basis of available data (toxicological, biochemical and other), establishment of any acceptable total daily intake of the iron is not necessary. On the other hand, because iron deficiency causes anaemia (Institute of Medicine 2002), recommended dietary allowance of iron for children (up to 8 years) and males/females is 40 and 45 mg/day, respectively.

Results concerning Zn and Fe levels presented in this article are similar to those published by Demirbas (1999) and Lombardi-Boccia et al. (2005) for chicken samples, Ferreira et al. (2000) and Lombardi-Boccia et al. (2005) for turkey samples, Tomović et al. (2011) for pork samples and Lombardi-Boccia et al. (2005) for beef samples.

The average copper concentration was between 0.6492 and 0.9831 mg/100 g in all samples investigated. Furthermore, the highest average concentrations of Cu were observed in pork samples. These values are higher than those determined by other authors (Demirbas 1999; Ferreira et al. 2000; Lombardi-Boccia et al. 2005; Tomović et al. 2011). The maximum Cu concentration for pork and beef samples has been proposed by the WHO (1993) as 7.0 and 1.6 mg/100 g wet wt, respectively. The Cu concentrations obtained from this study were under those values.

The mean levels of manganese in all samples varied from 0.1186 to 0.1481 mg/100 g, and the WHO (1993) recommends concentrations of manganese in meat samples to be between 0.1 and 0.8 mg/kg wet wt. These slightly higher manganese amounts might not present a health risk, since there is no information on

the carcinogenicity of manganese (Agency for Toxic Substances and Disease Registry 2004).

Mean concentrations of nickel in samples ranged from 0.0410 to 0.0510 mg/100 g, which are close to international standards (WHO 1993) (0.5 mg/kg wet wt). Highest average concentrations were obtained from beef (0.0505 mg/100 g) and pork (0.0510 mg/100 g) samples. This may be attributed to a lack of more careful handling practices and errors in raw material processing. The animal's long-term exposure to air pollution may also need to be taken into account, since the accumulation of heavy metals may be significant (Niemi et al. 1993). According to the Agency for Toxic Substances and Disease Registry (2004), nickel is a carcinogen and can cause respiration problems. The intake limits of nickel for children (1–3 years old) and men/women (19–70 years old) are 7 and 40 mg/day, respectively (WHO 1993; Demirezen and Uruc 2006).

The maximum allowed concentration of Cr according to WHO (1993) is 60 µg/kg wet wt, which is higher than the corresponding values reported in Table 3 and the database.

The levels of lead and cadmium reported in this study are below the recommended value (WHO 1993) for Pb and Cd (50 and 60 µg/kg wet wt, respectively) in meat samples. Cd levels in chicken samples were in agreement with those obtained by Demirbas (1999) and Lombardi-Boccia et al. (2005). For beef samples, obtained values are higher than those published by Demirezen and Uruc (2006). Pb content in beef and chicken samples are below those detected by other authors (Demirbas 1999; Lombardi-Boccia et al. 2005; Demirezen and Uruc 2006). There is no statistically significant difference in levels of Cu, Ni, Mn, Pb, Cd and Cr among meat type samples analysed.

Because there are no certified reference materials available for heavy metals in smoked meat samples, and considering the very low trace metal concentrations in samples, the accuracy of the developed procedure for metal determination was verified by spike recovery tests. The results presented in the database show recoveries between 92% and 112%, which could be considered suitable for heavy metal determination in meat samples.

Conclusions

Our work has shown that levels of the eight investigated heavy metals in analysed meats are in general below the safety limits established by the health authorities of the European Union. The exceptions are Mn and Ni. The amount of Mn in all samples is higher than the limit recommended by the WHO, whereas Ni concentration is higher than the allowed limit in certain number of samples. However, those

Table 3. Range and mean \pm SD (mg/100 g) of Fe, Cu, Ni, Cr, Pb, Mn, Zn and Cd in different smoked meat samples.

| Type of smoked meat | Fe | Cu | Ni | Cr | Pb | Mn | Zn | Cd |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Chicken | 0.9210–0.7284 | 0.6349–0.8715 | 0.0411–0.0529 | 0.0043–0.0057 | 0.0010–0.0015 | 0.1374–0.1623 | 0.6420–0.7846 | 0.0034–0.0053 |
| | 0.8126 \pm 0.113 | 0.7447 \pm 0.0958 | 0.0470 \pm 0.0048 | 0.0051 \pm 0.0005 | 0.0012 \pm 0.0002 | 0.1481 \pm 0.0102 | 0.7257 \pm 0.0715 | 0.0045 \pm 0.0008 |
| Pork | 0.6660–1.4876 | 0.6369–1.3570 | 0.0454–0.0545 | 0.0041–0.0059 | 0.0010–0.0013 | 0.0968–0.1558 | 0.9210–2.1625 | 0.0044–0.0055 |
| | 0.9438 \pm 0.3365 | 0.9831 \pm 0.2959 | 0.0510 \pm 0.004 | 0.0052 \pm 0.0007 | 0.0012 \pm 0.0001 | 0.1352 \pm 0.0242 | 1.5718 \pm 0.5093 | 0.0050 \pm 0.0005 |
| Beef | 0.8863–1.4376 | 0.4748–1.1203 | 0.0378–0.0677 | 0.0033–0.0045 | 0.0014–0.0019 | 0.1082–0.1936 | 3.9653–6.5978 | 0.0038–0.0068 |
| | 1.2154 \pm 0.2079 | 0.9053 \pm 0.2581 | 0.0505 \pm 0.0111 | 0.0038 \pm 0.0005 | 0.0017 \pm 0.0002 | 0.1410 \pm 0.0351 | 5.2726 \pm 0.9395 | 0.0050 \pm 0.0012 |
| Turkey | 0.5070–0.8740 | 0.2740–1.067 | 0.0341–0.0529 | 0.0029–0.0052 | 0.0011–0.0036 | 0.0875–0.1513 | 0.8800–1.8360 | 0.0034–0.0053 |
| | 0.6924 \pm 0.1652 | 0.6492 \pm 0.3491 | 0.041 \pm 0.0076 | 0.0042 \pm 0.0012 | 0.0027 \pm 0.0009 | 0.1186 \pm 0.0259 | 1.2456 \pm 0.3831 | 0.0042 \pm 0.0007 |

values still remain lower than the permitted daily intake levels for the elements. Pb and Cd, both infamous for their negative influence on human health, are present in small amounts that are well below WHO recommended values.

According to ANOVA, the content of Zn in beef samples was significantly higher than in samples of other meat types. Fe content in beef meat samples was significantly higher than the content of the metal in turkey meat samples. There is no statistically significant difference in the levels of Cu, Ni, Mn, Pb, Cd and Cr among different meat type samples.

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